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Thermodynamic functions of para-halostyrenes

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Recently Singh and Jaiswal (1970, 1971a, b) have studied the Raman spectra of para-halostyrenes and made a complete assignment of the observed lines. The present communication reports briefly thermodynamic functions calculated for the ideal gases of para-fluoro-, -chloro- and- bromostyrenes at the pressure of one atmosphere under the rigid rotor harmonic oscillator approximation as these values are expected to be much more accurate than those obtained by any experimental method.

INTRODUCTION

The total energy of a system is given by

$$\epsilon = \epsilon_{trans} + \epsilon_{rot} + \epsilon_{vib} + \epsilon_{elec}, \qquad \ldots \quad (1)$$

where the subscript *trans* stands for translational, *rot* for rotational, *vib* for vibrational and *elec* for electronic.

The partition function Q in terms of energy is given by

$$Q = \Sigma g_i \exp(-\epsilon_i/kT) = Q_{trans} \cdot Q_{rot} \cdot Q_{vib} Q_{elec}, \qquad \ldots \quad (2)$$

where g_i is the statistical weight, k is the Boltzmann constant and T is the absolute temperature

Thus one has to calculate each of the partition functions in equation (2) separately and then add together their contributions to thermodynamic functions. The electronic contribution is small and ignored because ϵ_{elec} is large compared to kT at ordinary temperatures. For the remaining partition functions, the standard expressions as given by Colthup *et al* (1964) have been used and their contributions to thermodynamic functions have been evaluated at various temperatures.

CALCULATIONS AND RESULTS

The molecules under study possess a single asymmetric off-balance top (vinyl group) attached to an essentially rigid frame (phenyl group). The rotation of the top is hindered by a two-fold potential barrier. If the internal rotation is entirely free, this vibrational degree of freedom has to be omitted from the vibrational partition function and instead an appropriate term is added to the

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rotational partition function. Its contribution to thermodynamic functions can be calculated by using formulae given by Herzberg (1945). But in the case of hindered internal rotation as for the present molecules it is necessary to apply certain modifications in their free internal rotation contributions. These modifications are possible with the help of Pitzer & Gwinn's tables (1942). Use of these tables needs a knowledge of the partition function of free internal rotation (Q_f) and hindering potential barrier height (V_0). To a good approximation Q_f for a single rotor is

$$Q_f = \frac{(8\pi^3 I_m kT)^{\frac{1}{2}}}{\sigma_t h}, \qquad \ldots (3)$$

where I_m is the reduced moment of inertia of the top, σ_t is the number of potential minima per revolution, also the symmetry number of internal rotation and other terms have their usual meanings. For para-halostyrenes $\sigma_t = 2$ and the value of V_0 is calculated (in harmonic oscillator approximation) by the relation

$$V_0 = \nu_t^2/4F, \qquad \ldots (4)$$

where $F = \frac{h}{8\pi^2 c I_m}$ in cm^{-1} and ν_t is observed torsional frequency which appears at 73, 67 and 67 cm^{-1} in para-fluoro-, -chloro- and -bromostyrenes, respectively.

Considering each molecule a planar one having C_s symmetry, principal moments of inertia I_x, I_y and I_z have been calculated where y and z axes are in the plane of the molecule and the x-axis is perpendicular to the plane. The structure data have been taken from Beckett & Pitzer (1946), Morer & Mulliken (1969) and International Tables for X-ray Crystallography (1962). The reduced moments of inertia have been calculated by the formula given by Pitzer (1946) for asymmetric off-balance top molecules. The moments of inertia, reduced moments of inertia, F and hindering potential barrier height V_0 thus calculated are given in table 1. The calculated values of the heat capacity, enthalpy function, entropy

Table 1. The calculated values of moment of inertia, reduced moment of inertia, F, and potential barrier heights of para-fluoro-, -chloro- and -bromostyrenes

Compound	Principal moments of inertia (10^{-39}gm cm^2)			Reduced moment of inertia (10^{-39}gm cm^2)	F (cm^{-1})	Barrier height V_0 (Kcal/mole)
	I_z	I_y	I_x			
p-F-styrene	16.70	82.84	99.54	2 1099	1.3258	2.873
p-Cl-styrene	16.90	117.42	134.32	2.1985	1.2725	2.521
p-Br-styrene	17.12	174.82	191.94	2 2688	1.2330	2.602

Table 2. Thermodynamic functions (in cal-mole/°K) of para-halostyrenes

Temp. °K	*p*-fluorostyrene				*p*-chlorostyrene				*p*-bromostyrene			
	$\frac{(H^0-E_0^0)}{T}$	$-\frac{(G^0-E_0^0)}{T}$	S^0	C_p^0	$\frac{(H^0-E_0^0)}{T}$	$-\frac{(G^0-E_0^0)}{T}$	S^0	C_p^0	$\frac{(H^0-E_0^0)}{T}$	$-\frac{(G^0-E_0^0)}{T}$	S^0	C_p^0
100	10.39	53.67	64.06	14.11	10.65	54.93	65 58	14 68	10.89	56.62	67.51	15.32
200	14.45	62 10	76.54	23.08	14.96	62.60	77 56	23.99	15.40	65 54	80.95	24.53
273.16	17.71	67.07	84 77	30.14	18.34	68.77	87.11	31.23	18.80	70.85	89.65	31.64
298.16	18.84	68.67	87.52	32.57	19.52	70 43	89.95	33.62	19.98	72.55	92.53	34.03
400	23.53	74.87	98.40	41.70	24.30	76.83	101 14	42.69	24.73	79 09	103.82	43.00
500	27.94	80.60	108.54	49.15	28.74	82.74	111.47	50.00	29.14	85.08	114.22	50.23
600	31.99	86.06	118.05	55.13	32.67	88.34	121 01	55.83	33.15	90 75	123.90	55.85
800	38.95	96.24	135.19	63.92	39.69	98 83	138.52	64 40	40.00	101 27	141.27	64.53
1000	44.54	105.58	150.12	69.98	45.29	108.19	153 48	70 33	45.52	110 80	156.33	70.41
1500	54.76	125.71	180.47	78.82	55.29	128.62	183 91	79.01	55.44	131.30	186.74	79 05

and free energy function at various temperatures ranging from 100-1500°K for the para-fluoro-, -chloro- and -bromostyrenes are given in table 2 and represented by curves in figures 1 and 2. Here E_0^0 is the energy of one mole of an ideal gas at absolute zero, H^0 is its enthalpy and G^0 is its free energy.

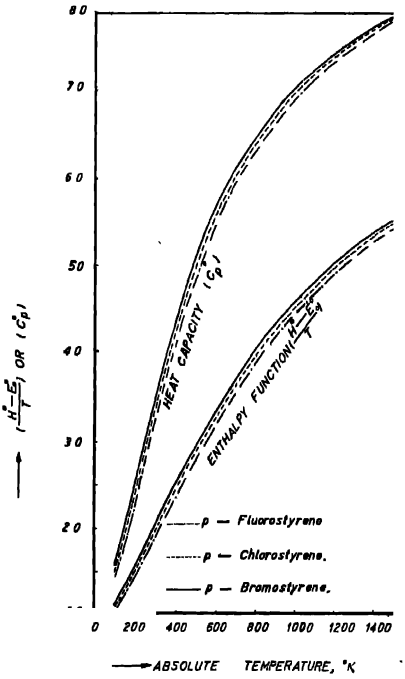

Figure 1. Variation of enthalpy function and heat capacity with absolute temperatures for para-fluoro-, -chloro- and -bromostyrenes.

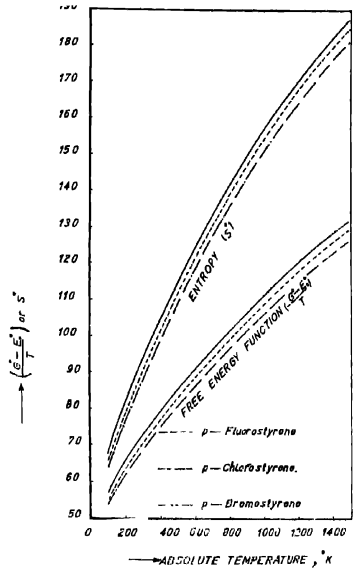

Figure 2 Variation of free energy function and entropy with absolute temperatures for para-fluoro-, -chloro- and -bromostyrenes

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